

Regular Article

Synthesis and characterization of cobalt-supported catalysts on modified magnetic nanoparticle: Green and highly efficient heterogeneous nanocatalyst for selective oxidation of ethylbenzene, cyclohexene and oximes with molecular oxygen



Ali Reza Faraji^{a,b,*}, Sima Mosazadeh^c, Fatemeh Ashouri^a

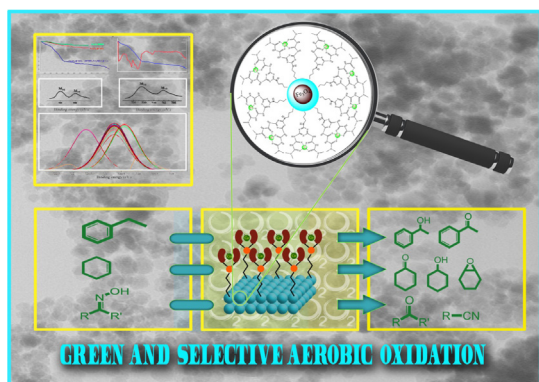
^aDepartment of Applied Chemistry, Faculty of Pharmaceutical Chemistry, Pharmaceutical Sciences Branch, Islamic Azad University (IAUPS), Tehran, Iran

^bYoung Researchers and Elite Club, Pharmaceutical Sciences Branch, Islamic Azad University (IAUPS), Tehran, Iran

^cDrug Delivery System Research Center, Pharmaceutical Sciences Branch, Islamic Azad University (IAUPS), Tehran, Iran

GRAPHICAL ABSTRACT

Oxidation of EB, CYHE and various oximes catalyzed by $\text{Fe}_3\text{O}_4@/\text{SiO}_2\text{-APTMS/CC/Met@Co(II)}$ under molecular oxygen.



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ABSTRACT

In this study, a new supported cobalt nanocatalyst has been described. The Fe_3O_4 magnetic nanoparticles (Fe_3O_4 MNPs) modified by SiO_2 /aminopropyl trimethoxy silane/cyanuric chloride ($\text{Fe}_3\text{O}_4@/\text{SiO}_2\text{-APTMS/CC}$) utilized for anchoring metformin-cobalt complex ($\text{Fe}_3\text{O}_4 \text{ Ms}@/\text{SiO}_2\text{-APTMS/CC/Met@Co(II)}$). The structure of novel complex well defined by elemental analysis, ICP, AAS, BET, FT-IR, EDX, SEM, TEM, DLS, XRD, TG-DTG, VSM and XPS. The catalytic efficiency of the synthesized cobalt nanocatalyst was studied in the oxidation of ethylbenzene (EB), cyclohexene (CYHE) and various oximes using molecular oxygen as eco-friendly oxidant and high catalytic activity and selectivity toward oxidation is observed. Selective aerobic oxidation of EB and CYHE and various oximes catalyzed by the cobalt nanocatalyst without any reducing agent by using N-hydroxyphthalimide (NHPI), gave acetophenone (AcPO), 2-cyclohexene-1-one and corresponding carbonyl compounds respectively, as major products. To achieve high level of efficiency of heterogeneous nanocatalyst, various parameters such as the ratio and amount of nanocatalyst/NHPI, reaction time, temperature and solvents were evaluated. The easily preparation from inexpensive and

* Corresponding author at: Department of Applied Chemistry, Faculty of Pharmaceutical Chemistry, Pharmaceutical Sciences Branch, Islamic Azad University (IAUPS), Tehran, Iran.

E-mail address: a.faraji@iaups.ac.ir (A.R. Faraji).

commercially available reagent, thermal stability, suitable performance in reusability, high efficiency and selectivity in oxidation reactions, short reaction time, easy recovery and separation from reaction mixture, are advantages of this novel catalyst.

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1. Introduction

The oxy-functionalization of benzylic and allylic C–H bonds of simple precursors such as ethylbenzene and cyclohexene represent a powerful method to the synthesis of value-added products such as acetophenone and cyclohexenone. These products which find widespread application as a flavoring agent in foods, fragrance in soaps and perfumes, as a solvent for plastics and resins and synthesis of a variety of chemical products such as pharmaceuticals insecticides, herbicides and fragrances [1,2].

In the past, this oxy-functionalization was performed using stoichiometric amount of chromium reagents such as pyridinium chlorochromate, pyridinium dichromate and chromic oxide-pyridine (Collins reagent), KMnO_4 and H_2O_2 [3–6] using *tert*-butyl hydroperoxide (TBHP) as oxidizing agents [7,8]. In many cases, the reactions conditions are harsh and unpleasant, the selectivity is unsatisfied and the reagent mixture is corrosive. Moreover, the catalyst is not reusable and a lot of wastes are produced. Therefore, for developing of environmentally-friendly technologies and processes, transition metals (such as Fe, Mn, Cu, V, Rh and Co) has been used which resolved mentioned disadvantages. In order to simplest separation of the catalyst from reaction mixture [9–12] and enhance its effective lifetime, various strategies such as immobilization of active centers on the surface of support can be employed. For example, encapsulation in zeolites [13–16], SBA-15 [17], Fe_3O_4 [18–20], the grafting on polymers or MCM-41 silica [20–24], the immobilization in polysiloxane membranes [25] and $\text{SiO}_2/\text{Al}_2\text{O}_3$ [26] have been used. Indeed surface coating and its modifications afford protection of the underlying materials from external erosion by chemical compound in system.

Among the active heterogeneous catalysts in organic reactions, magnetite Fe_3O_4 nanoparticles have attracted interest due to their low toxicity, thermal stability, high saturation magnetization, good biocompatibility, capability of being modified with reactive functional groups, easy and convenient isolation from reaction mixture and recycling [27,28]. Although, Fe_3O_4 nanoparticles (NPs) exhibit appropriate catalytic activity, but unprotected magnetic nanoparticles are found to be unstable, easily aggregate during catalytic reaction and highly sensitive to acidic and oxidative conditions [29]. The using of thin or thick non-magnetic materials to maintain individual particle stability and durability is suitable strategy for protection of Fe_3O_4 NPs. These protecting materials for selling not only stabilize the magnetic iron oxide NPs, but also can be used for the specific processes of further targeting functionalization and extended applications. The $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ -nHAlMo catalysts for epoxidation of olefins [30], core-multishell Fe_3O_4 - SiO_2 -GPS (GPS = 3-glycidoxypropyltrimethoxysilane) and Zn^{2+} coated with iminodiacetic acid [31], $\text{Fe}_3\text{O}_4@/\text{PDA}$ (PDA = poly dopamine) [32] and Fe_3O_4 - SiO_2 -GPS-CDI (CDI = 1,1-carbonyldiimidazole) for bio-application such as bone marrow transplant [33], are an example of supported Fe_3O_4 NPs. However, many of these metal-catalyzed systems are not compatible with the use of dioxygen as an oxidant and mostly need unfriendly oxidants to achieve appropriate catalytic performance [34–36]. Therefore, molecular oxygen preferred as a supreme oxidant due to its natural, highly economical, environmentally favorable and abundant characters [37,38].

Thus, in the field of heterogeneous nanocatalysis, searching for a suitable strategy in order to protect Fe_3O_4 nanoparticles is still a

tempting challenge. Herein, we described synthesis and structural characterization of new core-shell structured nanoparticles $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ -APTMS/CC/Met@Co(II). The catalytic efficacy of this thick functionalized Fe_3O_4 NPs as a heterogeneous catalyst is investigated in oxidation of ethylbenzene, cyclohexene and various oximes. The reaction has been done at aerobic and mild condition under oxygen source which exhibited excellent efficiency, stability and reusability of synthesized heterogeneous catalyst.

2. Experimental

2.1. Materials and instruments

Ferric chloride ($\text{FeCl}_3 \cdot 4\text{H}_2\text{O}$), ferrous chloride ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) and all reagents are obtained commercially and used as received without further drying or purification, but solvents were purified with standard methods. Inductively coupled plasma (ICP) measurements for cobalt content evaluation were performed using a Perkin-Elmer ICP/6500. Infrared spectrums were collected on KBr pallets using a JASCO FT/IR (680 plus) spectrometer and the position of an infrared band is given in reciprocal centimeters (cm^{-1}). Type and quantity of the resulting products from oxidation reactions were determined by a HP 6890/5973 GC/MS instrument and analyzed by a Shimadzu GC-16A gas chromatograph (GL-16A gas chromatograph with a $5\text{ m} \times 3\text{ mm}$ OV-17 column, 60–220 °C (10 °C/min), Inj. 230 °C, Det. 240 °C). For recording the thermal data, a Perkin-Elmer TG-DTA 6300 instrument at a heating rate of 15 °C/min and for elemental analysis a CHN-Rapid Heraeus elemental analyzer (Wellesley MA) were used. Before carrying out the nitrogen (99.999%) adsorption experiments the sample was out-gassed at 393 K for 14 h, then the experiment have been carried out at 76 K using a volumetric apparatus (Quantachrome NOVA automated gas sorption analyzer). The crystalline structures of samples were carried out by XRD analysis on a Bruker D8 Advance diffractometer with $\text{CuK}\alpha$ radiation at 40 kV and 20 mA. The specific surface areas were calculated, using the BET method. The images of scanning electron micrograph (SEM) and transmission electron microscopy (TEM) were taken using a Philips 501 microscope and Tecnai F30TEM operating at 300 kV, respectively. Samples for TEM observations were prepared by placing a drop containing the nanoparticles in a carbon-coated grid. In addition, energy dispersive X-ray (EDS) analysis was conducted on synthesized catalyst. Magnetization properties were passed out on a BHV-55 vibrating sample magnetometer (VSM). Size distribution (DLS) measured by Zetasizer Nano-ZS-90 (ZEN 3600, MALVERN instruments).

2.2. Preparation of cobalt-supported catalysts on modified magnetic nanoparticle

2.2.1. Preparation of super paramagnetic Fe_3O_4 nanoparticles

The Fe_3O_4 MNPs were synthesized according literature [39]. The aqueous solution of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (9.5 mmol) and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (4.7 mmol) in HCl (2 M) were mixed and deoxygenated by N_2 gas for 20 min. Then ammonia solution (50 mL, 37%) was added dropwise under vigorous stirring. The black solid appears when a reaction media reached to pH = 10. The mixture was stirred for 30 min at room temperature in N_2 atmosphere and then was heated at

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